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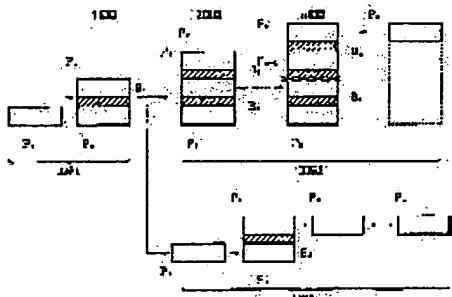
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(54) GAN SINGLE CRYSTAL AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain a high-quality GaN single crystal having enough thickness to be usable as a substrate singly.

CONSTITUTION: This GaN single crystal is such that the full width at half maximum in its double crystal X-ray rocking curve stands at 5-250sec and its thickness $\geq 80\mu$ m. This single crystal can be obtained by film formation, as buffer layers, of a substance good in the lattice conformity with the GaN single crystal on a substrate with at least its surface representing GaN single crystal and then by crystal growth of the aimed GaN. There are two alternatives in this production method depending on the method of removing the buffer layers: one method is as follows: the above-mentioned crystal growth cycle is repeated desired times and laminates are formed on the substrate P0 and then the respective buffer layers B1-Bn are removed at a time to obtain GaN single crystals P1-Pn; the other method is as follows: a buffer layer is removed at every cycle and the above-mentioned crystal growth cycle is repeated for a GaN single crystal singly at all times. These two alternative methods may be combined with each other.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the quality GaN single crystal which can be suitably used as GaN single crystal substrates, such as blue light emitting diode, and its manufacture method.

[0002]

[Description of the Prior Art] The appearance of the semiconductor device which can emit light for the short wavelength which reaches a blue shell ultraviolet-rays wavelength field is strongly searched for by the demand of multiple-colorizing in a luminescence display etc., and the demand of the improvement in data density in communication, record, etc. Its attention is paid to the GaN system single crystal which is the latus nitride of a band gap most in a III-V system compound semiconductor as a semiconductor material this blue - for ultraviolet luminescence devices. Since GaN has a transited [directly] type band structure, since the band gap in a room temperature is as large as about 3.4eV, it presents blue - ultraviolet luminescence possible [efficient luminescence], and it is a suitable material for the demand of the above-mentioned semiconductor device. However, since [that crystal-growth temperature of GaN is high and] the equilibrium vapor pressure of the nitrogen near crystal-growth temperature is high, it is very difficult to manufacture a large-sized single crystal for high quality from a melt. Therefore, growth of a GaN system single crystal was performed by the hetero-epitaxial grown method based on the non-static reaction by MOVPE (Metal Organic Vapor Phase Epitaxy) or MBE (Molecular Beam Epitaxy) to an excellent in thermal resistance silicon-on-sapphire, or SiC substrate top. On the other hand, the method of having formed membranes upwards on silicon on sapphire by making ZnO into a buffer layer, and growing up a GaN single crystal was indicated (for example, Applied physics letter Vol.61 (1992) p.2688), and production of a GaN substrate was attained in recent years. By growing up a homogeneous GaN system single crystal thin film on this GaN substrate, the quality of a GaN system single crystal thin film improved compared with the direct crystal growth to the above-mentioned silicon-on-sapphire top.

[0003]

[Problem(s) to be Solved by the Invention] However, by the conventional method using Above ZnO as a buffer layer, since membrane formation of ZnO to a silicon-on-sapphire top was what is depended on the sputtering method, this ZnO layer did not become a quality single crystal, but since the quality of this crystal structure influenced the following GaN single crystal layer, there was a problem that a quality GaN single crystal was not obtained. Moreover, the crystal quality of the GaN single crystal known conventionally Even if the quality, the full width at half maximum (full width at half-maximum of the double-crystal X-ray rocking curve) of 2 crystallization X-ray rocking curve About 100 secs, Mobility in a room temperature Although it was 600cm² / VS grade Since the method of growing up a crystal was MOVPE, it was difficult to separate a GaN single crystal from the substrate of a basis by not obtaining only about 5 micrometers of thickness, since it is very thin, for example, to use independently as a substrate of a semiconductor light emitting device. For this reason, when a GaN single crystal was used, it was obliged to use still in the state in the state where it was formed on the substrate of a basis.

Hereafter, on these specifications, "2 Full width at half maximum of a crystallization X-ray rocking curve" is only called "full width at half maximum." Moreover, although the thing of thickness with the GaN single crystal sufficient as a substrate grown up by HVPE (Hydride Vapor Phase Epitaxy) on the ZnO buffer layer was obtained as mentioned above, the full width at half maximum of the quality was the thing of low quality of 300 or more secs. That is, there was no GaN single crystal which has good quality and sufficient thickness simultaneously.

[0004] The purpose of this invention is a quality single crystal, and is offering the GaN single crystal which has such sufficient thickness that using as a substrate independently is possible. Other purposes of this invention are quality single crystals, and are offering the manufacture method of a GaN single crystal which can manufacture the GaN single crystal which has such sufficient thickness that using as a substrate independently is possible.

[0005]

[Means for Solving the Problem] Even if a GaN single crystal is the crystal structure of low quality by the conventional manufacture method, this invention person etc. Even if it is a crystal of those other than GaN(s), such as silicon on sapphire, these or as first crystal substrate By grid adjustment with a GaN single crystal carrying out thin film growth of the good matter, considering as a buffer layer besides, and carrying out the crystal growth of the GaN on this As that a more nearly quality GaN single crystal is obtained and the GaN single crystal concerned are used as a new substrate and a buffer layer and a GaN single crystal are again grown up on this It responded for repeating growing the buffer-layer matter and GaN epitaxially by turns, and the GaN single crystal was improved more in quality, found out that it could form in sufficient thickness, and completed this invention.

[0006] The GaN single crystal and its manufacture method of this invention have the following feature.

(1) The GaN single crystal whose thickness the full width at half maximum of 2 crystallization X-ray rocking curve is 5-250sec, and is 80 micrometers or more.

(2) The manufacture method of a GaN single crystal of having the process which was made carrying out thin film growth of the good matter of grid adjustment with a GaN single crystal, turned to the buffer layer up on the substrate whose front face is a GaN single crystal at least, is made carrying out the crystal growth of the GaN, and obtains a GaN single crystal.

(3) Make into 1 time of a crystal-growth cycle the process which was made to carry out thin film growth of the good matter of grid adjustment with a GaN single crystal, turned to the buffer layer up on the substrate whose front face is a GaN single crystal at least, is made to carry out the crystal growth of the GaN, and obtains a GaN single crystal. The manufacture method of the GaN single crystal characterized by removing each buffer layer after making 1 cycle repeat ***** form the above-mentioned crystal-growth cycle at least on the obtained GaN single crystal, and obtaining a GaN single crystal.

(4) Make into 1 time of a crystal-growth cycle the process which was made to carry out thin film growth of the good matter of grid adjustment with a GaN single crystal, turned to the buffer layer up on the substrate whose front face is a GaN single crystal at least, is made to carry out the crystal growth of the GaN, and obtains a GaN single crystal. The manufacture method of the GaN single crystal characterized by removing a buffer layer for the above-mentioned crystal-growth cycle for every [1 cycle repeat and] cycle at least, and obtaining a GaN single crystal by using the obtained GaN single crystal as a new substrate.

[0007]

[Function] The GaN single crystal of this invention is formed on a substrate by repeating membrane formation of a buffer layer, and the crystal growth of GaN in cycle by turns again. Many dislocation, a stacking fault, etc. which exist in a substrate disappear by the inside of the crystal-growth layer of GaN, and a buffer layer, or the interface of a substrate and a buffer layer or the interface of a buffer layer and a GaN crystal-growth layer. Therefore, whenever it performs this crystal-growth cycle once, it is thought that it will be asymptotically converged on single crystal structure which is specified on growth conditions if the quality of the single crystal structure of GaN improves and this is repeated infinite. If the GaN single crystal obtained by the manufacture method of this invention has good quality and it is required for it, it can be formed

even in the thickness of 80 micrometers or more, and will become desirable as a substrate of a semiconductor light emitting device especially.

[0008]

[Example] Hereafter, an example is given and this invention is explained more to a detail. The GaN single crystal of this invention has sufficient thickness of 80 micrometers or more, so that the full width at half maximum can show the value of 5-250sec and can use [quality] it as a substrate independently, as described above. In this invention, quality of a GaN single crystal was made into the quality of a GaN single crystal with the value of full width at half maximum shown by this method, using an X-ray diffraction method as a method for expressing numerically. An X-ray diffraction method is a method of using diffraction of the X-ray irradiated by the crystal. Also in it, by this invention, in order to raise the accuracy of measurement, it measured by the method of using two crystals. The X-ray diffraction method using two crystals is a method of evaluating the lattice constant of a sample precisely and evaluating the integrity of a crystal from the half-value width. In the quality evaluation of the GaN single crystal in this invention, the X-ray which carried out incidence from X line source was highly monochromatized by the 1st crystal, the GaN single crystal of the sample which is the 2nd crystal was irradiated, and full width at half maximum (full width at half-maximum) centering on the peak of the X-ray diffracted from this sample was measured. In X line source, it is Cukalpah1. It used and the X-ray was generated in 30kV and 10mA. germanium (400) was used for the 1st crystal for monochromatizing. Measurement shall be performed about the diffraction peak of GaN (0002), and the step interval of measurement shall be performed at 0.002 degrees.

[0009] The manufacture method which it shall mention later about the experimental value of the quality of the GaN single crystal by this invention, and can next obtain the GaN single crystal of such quality is explained. Drawing 1 is drawing showing typically an example of the formation process of the GaN single crystal by the manufacture method of this invention. the first substrate P0 whose front face is a GaN single crystal at least as this draftsman shows the manufacture method of the GaN single crystal of this invention most briefly to 1 grid adjustment with a GaN single crystal deposits the good matter upwards — making — buffer layer B1 ** — it turned up, the crystal growth of the GaN is carried out, and a GaN single crystal is obtained

[0010] The manufacture method of the GaN single crystal of this invention is the substrate P1 of the layered product formed by this draftsman at the process 1 again as shown in 2. Grid adjustment with a GaN single crystal turns the thin film growth of the good matter up, and it is buffer-layer B-2. Substrate P2 which formed upwards, is made to carry out the crystal growth of the GaN, and consists of a GaN single crystal It is made to form. counting a process 1 with the 1st time, and repeating such a process n times in cycle — the best layer — GaN single crystal Pn each buffer layer accumulated till then after growing up — at once — removing — GaN single crystal P1 -Pn dissociating — many — it is the method of using as the GaN single crystal of several sheets although the crystal quality of GaN obtained improves by the above-mentioned method whenever it increases the number of cycles, after improvement in crystal quality reaches equilibrium — rather — many — it will become useful as several substrates production technology

[0011] Further, as shown in 3, this draftsman the manufacture method of the GaN single crystal of this invention Buffer layer B1 of a process 1 It removes and is the GaN single crystal P0 and P1. It dissociates. Independent substrate P1 of a GaN single crystal It obtains and is the substrate P1 concerned. Grid adjustment with a GaN single crystal turns the thin film growth of the good matter up, and it is buffer-layer B-2. It formed upwards, the crystal growth of the GaN is carried out, and it is buffer-layer B-2. It removes and is the GaN single crystal P1 and P2. It dissociates. The GaN single crystal Pn is obtained by counting a process 1 with the 1st time, and repeating such a process n times in cycle. That is, this method is the method of always using the GaN single crystal which removes the buffer layer which became the foundation of the crystal growth whenever the GaN single crystal newly obtained carried out the crystal growth for every cycle, and is newly obtained as a GaN independent single crystal. After improvement in crystal quality reaches equilibrium like the above-mentioned process 2 also in this method, it uses as a product material, and also two GaN single crystals separated by removing a buffer layer may be

respectively used again as a substrate of the following GaN crystal-growth cycle.

[0012] Moreover, it considers as the method of compounding suitably two methods shown in processes 2 and 3, and how to remove a buffer layer to every number of times k with an arbitrary crystal-growth cycle can be considered. You may choose freely the arbitrary number of times k in this case.

[0013] As mentioned above, by repeating a crystal-growth cycle, whenever the crystal structure of GaN performs this crystal-growth cycle once, quality improves, and the manufacture method of the GaN single crystal of this invention is the GaN single crystal Pn very quality to the n-th desired number of times. It is obtained.

[0014] Thin film growth of a buffer layer has the desirable forming-membranes method which can grow epitaxially especially to upgrading of the GaN single crystal obtained, although the well-known forming-membranes method and a crystal-growth method are used. Moreover, the forming-membranes method which can grow epitaxially is desirable to upgrading like [the method of carrying out the crystal growth of the GaN to up to a buffer layer] thin film growth of a buffer layer.

[0015] Epitaxial growth is the method of growing up the same matter as this, or the matter of the same crystal structure on a crystal substrate as a single crystal with which the sense of the crystallographic axis was equal to the sense of the crystallographic axis of a substrate. In this invention, the forming-membranes method for growing the matter used as GaN or a buffer layer epitaxially is the most desirable, and VPE (Vapor Phase Epitaxy), HVPE, MOVPE, MBE, GS-MBE (Gas Source MBE), CBE (Chemical beam Epitaxy), etc. are mentioned especially.

[0016] Especially the number of times n that repeats the above-mentioned crystal-growth cycle is not limited, and although it may determine the number of times of a cycle according to the number of sheets of the GaN crystal substrate to need, corresponding to the quality of the GaN crystal for which it asks, in order to use as a GaN crystal substrate for the usual semiconductor devices, it serves as crystal quality sufficient by two - about 5 times.

[0017] Although the method of removing the above and the buffer layer used as the foundation of the crystal growth of GaN may be what method as long as it is the method that the obtained GaN single crystal may be separated, its chemical removal method by the acid etc. is effective.

[0018] What has grid adjustment good [the matter used for the above-mentioned buffer layer] with a GaN single crystal is used. A GaN single crystal and the good matter of the affinity made from a grid say that in which the lattice constant of the a-axis in a crystal lattice also has the Ur Die Zeit type crystal structure which is less than **5% preferably less than **10% to it of a GaN single crystal. ZnO is mentioned as a desirable example of the matter with which are satisfied of this. The lattice constant (the length of a unit lattice) of the a-axis of ZnO is 3.2496A, and since it is equipped with +1.9% and the lattice constant approximated very much to the lattice constant of 3.189A of the a-axis of GaN and the good crystal growth of GaN can perform it, it is desirable. Moreover, the etching removal nature of ZnO by the acid is good, and suitable for it as matter used for a buffer layer also at this point. The thickness of a buffer layer has 0.01 micrometers - desirable about 100 micrometers.

[0019] The first substrate P0 That whose front face is a GaN single crystal at least is used. That is, they are the independent substrate of the GaN single crystal with which the whole consists only of GaN substantially, or the substrate [as / only whose front face which has a GaN single crystal layer on the front face by the side of the buffer stratification is a GaN single crystal]. In the case of the latter, what has the thermal resistance good as base-material matter which supports a GaN single crystal layer to the growth temperature (1000-1100 degrees C) of a GaN single crystal is desirable, for example, a sapphire crystal substrate, Si substrate, crystal, a ZnO substrate, a SiC substrate, etc. are illustrated. Formation of the GaN single crystal layer to these base-materials matter top can be performed by the hetero-epitaxial grown method based on the non-static reaction by the MOVPE method, the MBE method, etc.

[0020] [A manufacture experiment of a GaN single crystal and quality check experiment] Next, a GaN single crystal is actually manufactured by the manufacture method of the GaN single crystal of this invention, and the result which checked the quality is shown.

As the example of the one example experiment of an experiment shows to the process 2 in

drawing 1 as a method of repeating the crystal-growth cycle in the manufacture method of the GaN single crystal of the above-mentioned this invention, it is the first substrate P0. Up, the buffer layer and the GaN single crystal were grown up one by one, and turned the laminating, and it considered as the method of removing each buffer layer at once finally, and separating a GaN single crystal. The first substrate P0 If carried out, the substrate which grew the GaN single crystal layer epitaxially by the MOVPE method was used on the sapphire crystal base material. The buffer layer set thickness to 0.2 micrometers, and set material to ZnO. A crystal-growth cycle shall be repeated 5 times. The GaN single crystal P1 – P5 which are formed in crystal-growth cycle each time All thickness aimed at 300 micrometers. GaN single crystal P5 obtained at the end When full width at half maximum was measured, it was 29sec and the thickness was 305 micrometers.

[0021] In the example of the two example experiment of an experiment, it replaced with the method of repeating the crystal-growth cycle in the above-mentioned example 1 of an experiment, as shown in the process 3 in drawing 1 , whenever the GaN single crystal grew epitaxially, the buffer layer in front of it was removed, and the completely same GaN single crystal as the example 1 of an experiment was produced except having always used the new substrate as the GaN independent single crystal of one sheet. GaN single crystal P5 obtained at the end Full width at half maximum of quality was 28sec(s), and the thickness was 289 micrometers.

[0022] In the example of the three example experiment of an experiment, the completely same GaN single crystal as the example 2 of an experiment was produced except having used the substrate of three layers which consists of silicon on sapphire, a buffer layer of AlN (aluminum nitride), and a GaN single crystal as first substrate in the above-mentioned example 2 of an experiment. The manufacture process of the substrate of three layers is explained briefly. On 300 micrometers in thickness, and the area 5cmx5cm sapphire crystal substrate, AlN was grown epitaxially to the thickness of 500A by the MOVPE method as a buffer layer, material gas was changed with the state, the GaN single crystal was grown epitaxially to the thickness of 2 micrometers by the same MOVPE method, it considered as the surface, and the substrate of three layer structures with a total thickness of about 302 micrometers which consists of a sapphire crystal substrate, an AlN buffer layer, and a surface of a GaN single crystal GaN single crystal P5 obtained at the end by this experiment Full width at half maximum of quality was 25sec(s), and the thickness was 295 micrometers.

[0023] the example of the four example experiment of an experiment — the above-mentioned example 2 of an experiment — setting — the first substrate P0 ***** — as the material (BeO) of the buffer layer in each cycle at the time of repeating the crystal-growth cycle of a GaN single crystal using the same substrate of three layers as the example 3 of an experiment — 0.13 (ZnO) 0.87 The completely same GaN single crystal as the example 2 of an experiment was produced except having used. GaN single crystal P5 obtained at the end by this experiment Full width at half maximum of quality was 28sec(s), and the thickness was 301 micrometers.

[0024] In the example of the five example experiment of an experiment, in order to compare with the quality of the GaN single crystal by this invention, the quality of the GaN single crystal by the conventional manufacture method was investigated. On 300 micrometers in thickness, and the area 5cmx5cm sapphire crystal substrate, the buffer layer with a made from ZnO by the sputtering method thickness of 0.6 micrometers was formed, and the GaN single crystal was grown epitaxially to 250 micrometers in thickness by HVPE on it. The full width at half maximum of the quality of this GaN single crystal was 420sec(s).

[0025] It was checked that the manufacture method of the GaN single crystal of this invention can manufacture the quality GaN single crystal which is not in the former, and it is possible to manufacture in sufficient thickness to use a GaN single crystal as an independent substrate so that clearly [in the above-mentioned experimental result].

[0026] Such a quality and thick GaN single crystal obtained by the manufacture method of this invention is preferably used for uses, such as semiconductor light emitting devices, such as light emitting diode (Light Emitting Diode), laser diode (LD), and super luminescence diode, and an electron device. In a semiconductor light emitting device, it is using the GaN single crystal of this

invention as a substrate, and manufacture of Light Emitting Diode, LD, etc. which have the structure of the same electrode section as the conventional red Light Emitting Diode etc. is attained. What carries out blue luminescence also especially in these is important. Moreover, the efficiency of luminescence of the semiconductor light emitting device will become higher.

[0027] [Quality check experiment of Light Emitting Diode using the GaN single crystal by this invention] Light Emitting Diode using the GaN single crystal obtained by the manufacture method of this invention as a substrate was actually manufactured, and the quality was checked. Moreover, Light Emitting Diode which uses respectively the GaN single crystal and sapphire crystal of quality as a substrate conventionally was manufactured, and it compared with the quality of Light Emitting Diode which uses the GaN single crystal of this invention as a substrate. As a GaN single crystal of quality, full width at half maximum used the thing of 300sec(s) conventionally. The quality of Light Emitting Diode evaluated about early brightness and an early life. The life measured the brightness after carrying out continuation luminescence by 20mA current for 2000 hours into temperature the atmosphere of 85% of humidity of 85 degrees C, and it asked for the decreasing rate to the brightness in early stages of the brightness, and A and less than two to five decreasing rate % was divided into B, and 5 – 10% of decreasing rates was divided into C and three ranks for less than 2% of decreasing rates. The structure of Light Emitting Diode used as the substrate the GaN single crystal obtained by the manufacture method of this invention, and considered the n-AlGaN clad layer, the InGaN barrier layer of undoping, and the p-AlGaN clad layer as the double heterojunction type composition made to come to grow up one by one on this substrate. The full width at half maximum of the quality of the substrate of the GaN single crystal by this invention is three kinds, 30sec(s), 100sec, and 250sec. All thickness is 280 micrometers. Moreover, the composition ratio of InGaN of a barrier layer considered as two kinds, In0.15Ga0.85N and In0.25Ga0.75N, and experimented by creating a light emitting device about InGaN of each composition ratio. This experimental result is shown in the next tables 1 and 2.

[0028]

[Table 1]

活性層の組成比が $In_{0.15}Ga_{0.85}N$ である LED

の輝度と寿命の比較

基板	FWHM (sec)	初期の輝度 (candela)	寿命
GaN	30	1.8	A
GaN	100	1.4	A
GaN	250	1.2	B
GaN サファイア	800 —	1.1 1.0	B C

[0029]

[Table 2]

活性層の組成比がIn_{0.25}Ga_{0.75}NであるLED
の輝度と寿命の比較

基板	FWHM (sec)	初期の輝度 (candela)	寿命
GaN	30	2.9	A
GaN	100	2.5	A
GaN	250	2.2	B
GaN サファイア	300 —	2.2 2.0	B C

[0030] As shown in Tables 1 and 2, it is early brightness and the point of a life and, as for Light Emitting Diode using the quality GaN single crystal by this invention as a substrate, it turns out that it is Light Emitting Diode superior to the conventional thing.

[0031] Moreover, the following phenomenon has been checked about LD. In the conventional LD which uses a sapphire crystal as a substrate, since the state of the field of the GaN system compound semiconductor layer which will not be in the mirror-plane state where a substrate side is desirable, but is formed in the substrate side since it is the matter with a sapphire crystal difficult for formation of a cleavage plane followed the state of a substrate side, the reflector desirable for LD was not able to be formed. However, since it had thickness quality [the GaN single crystal by this invention], and sufficient, it became easy to obtain the cleavage plane by using a GaN single crystal as a substrate. Moreover, since crystal quality was inferior, although induced emission by current pouring has not been attained in LD using the conventional GaN system compound semiconductor, when constituted and experimented in the stripe laser of the Fabry-Perot resonator using the quality GaN single crystal by this invention as a substrate, induced emission was checked in the room temperature.

[0032]

[Effect of the Invention] As explained in full detail above, the GaN single crystal of this invention is simultaneously equipped with the crystal quality which was not in the former, and sufficient thickness. Moreover, the manufacture method of this invention can offer suitably the GaN single crystal simultaneously equipped with such quality and sufficient thickness. Therefore, in order to obtain Light Emitting Diode which presents efficient blue luminescence, and ultraviolet-rays laser diode or a heat-resistant good semiconductor device, the substrate of a suitable GaN single crystal is offered and the thing of it can be carried out. Moreover, the manufacture method of this invention can manufacture efficiently the improvement in the crystal quality of a GaN single crystal, and not only acquisition of thickness but several quality GaN many single crystals, and is industrial very important technology.

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CLAIMS

[Claim(s)]

[Claim 1] The GaN single crystal whose thickness the full width at half maximum of 2 crystallization X-ray rocking curve is 5-250sec, and is 80 micrometers or more.

[Claim 2] The manufacture method of a GaN single crystal of having the process which was made carrying out thin film growth of the good matter of grid adjustment with a GaN single crystal, turned to the buffer layer up on the substrate whose front face is a GaN single crystal at least, is made carrying out the crystal growth of the GaN, and obtains a GaN single crystal.

[Claim 3] The manufacture method of the GaN single crystal characterized by to remove each buffer layer after making into 1 time of a crystal-growth cycle the process which was made to carry out thin film growth of the good matter of grid adjustment with a GaN single crystal, turned to the buffer layer up on the substrate whose front face is a GaN single crystal at least, is made to carry out the crystal growth of the GaN, and obtains a GaN single crystal and making 1 cycle repeat ***** form the above-mentioned crystal-growth cycle at least on the obtained GaN single crystal, and to obtain a GaN single crystal.

[Claim 4] The process which was made to carry out thin film growth of the good matter of grid adjustment with a GaN single crystal, turned to the buffer layer up on the substrate whose front face is a GaN single crystal at least, is made to carry out the crystal growth of the GaN, and obtains a GaN single crystal is made into 1 time of a crystal-growth cycle. The manufacture method of the GaN single crystal characterized by removing a buffer layer for the above-mentioned crystal-growth cycle for every [1 cycle repeat and] cycle at least, and obtaining a GaN single crystal by using the obtained GaN single crystal as a new substrate.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the ** type view showing an example of the process of the manufacture method of the GaN single crystal by this invention.

[Description of Notations]

P0 The first substrate

P1 -Pn GaN single crystal

B1 -Bn Buffer layer

[Translation done.]

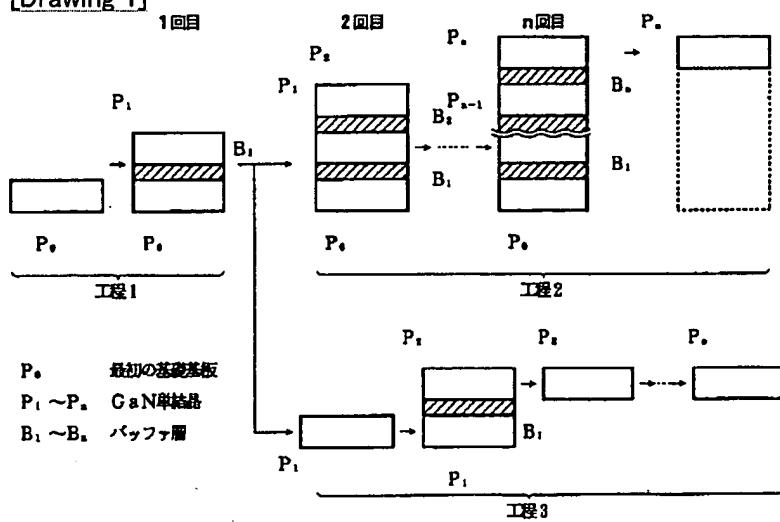
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DRAWINGS

[Drawing 1]



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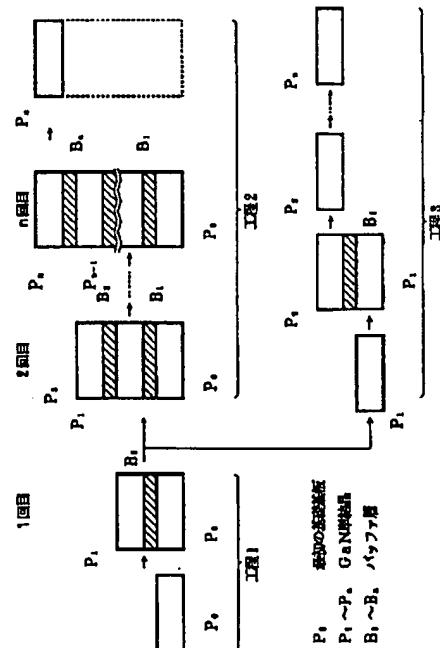
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(54)【発明の名称】 GaN単結晶およびその製造方法

(57)【要約】

【目的】 高品質な単結晶で、かつ、単独で基板として用いることが可能なほど十分な厚みを有するGaN単結晶とその製造方法を提供すること。

【構成】 2結晶法X線ロッキングカーブの半値全幅が5~250sec、かつ、厚みが80μm以上のGaN単結晶である。少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を成膜しバッファ層とした上に目的のGaNを結晶成長させる工程を有する製造方法によって製造される。この製造方法はバッファ層の除去法によって分けられる。最初の基板P₁上に上記結晶成長サイクルを所望の回数繰り返して積層物を形成させた後に各バッファ層B₁~B_nを一度に除去しGaN単結晶P₁~P_nを得る方法。1サイクル毎にバッファ層を除去し、常にGaN単独の単結晶として上記結晶成長サイクル繰り返す方法。そして、これらが複合された方法である。



【特許請求の範囲】

【請求項1】 2結晶法X線ロッキングカーブの半値全幅が5～250secであり、かつ、厚みが80μm以上であるGaN単結晶。

【請求項2】 少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を薄膜成長させてバッファ層とした上にGaNを結晶成長させてGaN単結晶を得る工程を有するGaN単結晶の製造方法。

【請求項3】 少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を薄膜成長させてバッファ層とした上にGaNを結晶成長させてGaN単結晶を得る工程を1回の結晶成長サイクルとし、得られたGaN単結晶上に上記結晶成長サイクルを少なくとも1サイクル繰り返して積層物を形成させた後に各バッファ層を除去し、GaN単結晶を得ることを特徴とするGaN単結晶の製造方法。

【請求項4】 少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を薄膜成長させてバッファ層とした上にGaNを結晶成長させてGaN単結晶を得る工程を1回の結晶成長サイクルとし、得られたGaN単結晶を新たな基板として上記結晶成長サイクルを少なくとも1サイクル繰り返し、かつ1サイクル毎にバッファ層を除去し、GaN単結晶を得ることを特徴とするGaN単結晶の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、青色発光ダイオード等のGaN単結晶基板として好適に用いることができる高品質なGaN単結晶、および、その製造方法に関する。

【0002】

【従来の技術】 発光ディスプレイ等における多色化の要求や、通信・記録等におけるデータ密度向上の要求によって、青色から紫外線波長領域に至る短波長の発光が可能な半導体デバイスの出現が強く求められている。この青色～紫外発光デバイス用の半導体材料として、III-V系化合物半導体では最もバンドギャップの広い空気化であるGaN系単結晶が着目されている。GaNは、直接遷移型バンド構造を有するために高効率の発光が可能であり、かつ、室温でのバンドギャップが約3.4eVと大きいため青色～紫外発光を呈し、上記半導体デバイスの要求に好適な材料である。しかし、GaNは、結晶成長温度が高く、また結晶成長温度付近での空素の平衡蒸気圧が高いため、融液から高品質で大型の単結晶を製造することは極めて困難である。従って、GaN系単結晶の成長は、耐熱性に優れたサファイア基板またはSiC基板上への、MOVPE (Metal Organic Vapor Phase Epitaxy) またはMBE (Molecular Beam Epitaxy) による非平衡反応に基づくヘテロエピタキシャル成長法によって行われていた。これに対して、近年、ZnOをバ

ッファ層としてサファイア基板上に成膜した上にGaN単結晶を成長させる方法が開示され（例えば、Applied physics letter Vol.61 (1992) p.2688）、GaN基板の作製が可能になった。このGaN基板上に同質のGaN系単結晶薄膜を成長させることによって、上記サファイア基板上への直接的な結晶成長にくらべGaN系単結晶薄膜の品質は向上した。

【0003】

【発明が解決しようとする課題】 ところが、上記ZnOをバッファ層として用いる従来の方法では、サファイア基板上へのZnOの成膜がスパッタリング法によるものであるため、該ZnO層は高品質の単結晶とはならず、この結晶構造の品質が次のGaN単結晶層に影響するために高品質なGaN単結晶が得られないという問題があった。また、従来知られていたGaN単結晶の結晶品質は、最も高品質なものであっても、2結晶法X線ロッキングカーブの半値全幅 (full width at half-maximum of the double-crystal X-ray rocking curve) が100sec程度、室温でのMobilityは600cm²/Vs程度であったが、結晶を成長させる方法がMOVPEであるために膜厚が5μm程度しか得られず非常に薄いので、GaN単結晶をもとの基板から分離し、例えば半導体発光素子の基板として、単独に用いることは困難であった。このため、GaN単結晶を利用する場合は、もとの基板上に形成された状態のまま用いることを余儀なくされていたのである。以下、本明細書では、「2結晶法X線ロッキングカーブの半値全幅」を単に「半値全幅」という。また、上記のようにZnOバッファ層上に、HYPE (Hydride Vapor Phase Epitaxy) によって成長させたGaN単結晶は、基板としては十分な厚みのものが得られていたが、その品質は半値全幅が300sec以上の低品質のものであった。即ち、良好な品質と十分な厚みと同時に有するGaN単結晶はなかったのである。

【0004】 本発明の目的は、高品質な単結晶で、かつ、単独で基板として用いることが可能なほど十分な厚みを有する、GaN単結晶を提供することである。本発明の他の目的は、高品質な単結晶で、かつ、単独で基板として用いることが可能なほど十分な厚みを有するGaN単結晶の製造が可能な、GaN単結晶の製造方法を提供することである。

【0005】

【課題を解決するための手段】 本発明者等は、GaN単結晶が従来の製造方法による低品質の結晶構造であっても、あるいはサファイア基板等のようなGaN以外の結晶であっても、これらを最初の結晶基板として、この上にGaN単結晶との格子整合性が良好な物質を薄膜成長させてバッファ層とし、この上にGaNを結晶成長させることによって、より高品質のGaN単結晶が得られることが、および当該GaN単結晶を新たな基板とし、再び

この上にバッファ層・GaN単結晶を成長させるというように、バッファ層物質とGaNとを交互にエピタキシャル成長させることを繰り返すに応じてGaN単結晶がより高品質化され、十分な厚みに形成し得ることを見出し本発明を完成した。

【0006】本発明のGaN単結晶およびその製造方法は次の特徴を有するものである。

(1) 2結晶法X線ロッキングカーブの半値全幅が5~250secであり、かつ、厚みが80μm以上であるGaN単結晶。

(2) 少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を薄膜成長させてバッファ層とした上にGaNを結晶成長させてGaN単結晶を得る工程を有するGaN単結晶の製造方法。

(3) 少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を薄膜成長させてバッファ層とした上にGaNを結晶成長させてGaN単結晶を得る工程を1回の結晶成長サイクルとし、得られたGaN単結晶上に上記結晶成長サイクルを少なくとも1サイクル繰り返して積層物を形成させた後に各バッファ層を除去し、GaN単結晶を得ることを特徴とするGaN単結晶の製造方法。

(4) 少なくとも表面がGaN単結晶である基板上にGaN単結晶との格子整合性の良好な物質を薄膜成長させてバッファ層とした上にGaNを結晶成長させてGaN単結晶を得る工程を1回の結晶成長サイクルとし、得られたGaN単結晶を新たな基板として上記結晶成長サイクルを少なくとも1サイクル繰り返し、かつ1サイクル毎にバッファ層を除去し、GaN単結晶を得ることを特徴とするGaN単結晶の製造方法。

【0007】

【作用】本発明のGaN単結晶は、基板上にバッファ層の成膜とGaNの結晶成長とを交互に、また、サイクリ的に繰り返すことによって形成される。基板中に存在している多くの転位、積層欠陥などは、GaNの結晶成長層内、バッファ層内、または基板とバッファ層との界面、またはバッファ層とGaN結晶成長層との界面で消滅する。従って、該結晶成長サイクルを1回行なう毎に、GaNの単結晶構造の品質は向上し、これを限りなく繰り返せば、成長条件で規定されるような単結晶構造に漸近的に収束するものと思われる。本発明の製造方法によって得られるGaN単結晶は品質が良好であり、また、必要ならば80μm以上の厚みにまで形成することが可能であり、特に半導体発光素子の基板として好ましいものとなる。

【0008】

【実施例】以下、実施例を挙げて本発明をより詳細に説明する。本発明のGaN単結晶は、上記したように、その半値全幅が5~250secの値を示す高品質なものであり、かつ、単独で基板として用いることができる

程、充分な厚み80μm以上を有するものである。本発明では、GaN単結晶の品質を数値で表すための方法としてX線回折法を用い、この方法によって示される半値全幅の値をもってGaN単結晶の品質とした。X線回折法は、結晶に照射されたX線の回折を利用する方法である。そのなかでも、本発明では、その測定精度を向上させるために、2結晶を用いる方法によって測定をおこなった。2結晶を用いるX線回折法は、試料の格子定数を精密に評価し、その半値幅から結晶の完全性を評価する方法である。本発明におけるGaN単結晶の品質評価においては、X線源から入射したX線を第1結晶により高度に単色化して、第2結晶である試料のGaN単結晶に照射し、この試料から回折するX線のピークを中心とするFWHM (full width at half-maximum) を測定した。X線源にはCuK α_1 を用い、30kV、10mAでX線を発生させた。単色化のための第1結晶には、Ge(400)を用いた。測定は、GaN(0002)の回折ピークについて行い、測定のステップ間隔は0.02°で行うものとした。

【0009】本発明によるGaN単結晶の品質の実験値については後述するものとし、次にこのような品質のGaN単結晶を得ることが可能な製造方法を説明する。図1は本発明の製造方法によるGaN単結晶の形成工程の一例を模式的に示す図である。本発明のGaN単結晶の製造方法は、最も簡単には、同図工程1に示すように、少なくとも表面がGaN単結晶である最初の基板P₁上にGaN単結晶との格子整合性が良好な物質を堆積させてバッファ層B₁とした上にGaNを結晶成長させてGaN単結晶を得るものである。

【0010】本発明のGaN単結晶の製造方法は、また、同図工程2に示すように、工程1で形成された積層体の基板P₁上にGaN単結晶との格子整合性が良好な物質を薄膜成長させてバッファ層B₂を形成した上にGaNを結晶成長させGaN単結晶よりなる基板P₂を形成させる。この様な工程を、工程1を1回目と数えてサイクリ的にn回繰り返すことによって最上層にGaN単結晶P_nが成長した後に、それまで累積した各バッファ層を一度に除去し、GaN単結晶P₁~P_nを分離して多数枚のGaN単結晶とする方法である。上記方法では、サイクル数を増やす毎に、得られるGaNの結晶品質は向上するが、結晶品質の向上が平衡状態に達した後は、むしろ多数枚の基板作製技術として有用なものとなる。

【0011】本発明のGaN単結晶の製造方法は、さらに、同図工程3に示すように、工程1のバッファ層B₁を除去してGaN単結晶P₀、P₁を分離し、GaN単結晶の単独基板P₁を得、当該基板P₁上にGaN単結晶との格子整合性が良好な物質を薄膜成長させてバッファ層B₂を形成した上にGaNを結晶成長させ、バッファ層B₂を除去してGaN単結晶P₁、P₂を分離す

る。この様な工程を、工程1を1回目と数えてサイクリ的にn回繰り返すことによってGaN単結晶P₀が得られる。即ち、本方法は新たに得られるGaN単結晶が結晶成長する度に、その結晶成長の基礎となったバッファ層を1サイクル毎に除去し、新たに得られるGaN単結晶を常にGaN単独の単結晶とする方法である。この方法においても上記工程2と同様に、結晶品質の向上が平衡状態に達した後は、バッファ層を除去して分離される2つのGaN単結晶は、製品材料として利用する他に、各々次のGaN結晶成長サイクルの基板として再び利用してもよい。

【0012】また、工程2、3に示した2つの方法を適当に複合する方法として、結晶成長サイクルの任意の回数kごとにバッファ層を除去する方法が考えられる。この場合の任意の回数kは自由に選択してよい。

【0013】上記のように、本発明のGaN単結晶の製造方法は、結晶成長サイクルを繰り返すことによって、GaNの結晶構造が該結晶成長サイクルを1回行なう毎に品質が向上し、所望の回数n回目に、極めて高品質なGaN単結晶P₀が得られるというものである。

【0014】バッファ層の薄膜成長は、公知の成膜法や結晶成長法が用いられるが、特にエピタキシャル成長可能な成膜法が、得られるGaN単結晶の品質向上に対して好ましい。また、バッファ層上へGaNを結晶成長させる方法も、バッファ層の薄膜成長と同様に、エピタキシャル成長可能な成膜法が品質向上に対して好ましい。

【0015】エピタキシャル成長は、結晶基板上にこれと同一物質あるいは同一結晶構造の物質を、その結晶軸の向きが基板の結晶軸の向きにそろった単結晶として成長させる方法である。本発明においては、GaNやバッファ層となる物質をエピタキシャル成長させる成膜法が最も好ましく、特にVPE(Vapor Phase Epitaxy)、HVPE、MOVPE、MBE、GS-MBE(Gas Source MBE)、CBE(Chemical beam Epitaxy)等が挙げられる。

【0016】上記結晶成長サイクルを繰り返す回数nは、特に限定されるものではなく、求めるGaN結晶の品質に応じて、また、必要とするGaN結晶基板の枚数に応じてサイクル回数を決定してよいが、通常の半導体デバイス用のGaN結晶基板として用いるには、2回～5回程度で十分な結晶品質となる。

【0017】上記、GaNの結晶成長の基礎となったバッファ層を除去する方法は、得られたGaN単結晶を分離しうる方法であればどのような方法であってもよいが、酸等による化学的な除去方法が有効である。

【0018】上記バッファ層に用いられる物質は、GaN単結晶との格子整合性が良好なものが用いられる。GaN単結晶と格子整合性の良好な物質とは、結晶格子におけるa軸の格子定数が、GaN単結晶のそれに対して±10%以内、好ましくは±5%以内であるウルツァイ

ト型の結晶構造も持つものを使う。これを満足する物質の好ましい例として、ZnOが挙げられる。ZnOのa軸の格子定数(単位格子の長さ)は3.2496Åであり、GaNのa軸の格子定数3.189Åに対して+1.9%と、非常に近似した格子定数を備えており、良好なGaNの結晶成長が行い得るので望ましい。また、ZnOは酸によるエッチング除去性が良好であり、この点でも、バッファ層に用いる物質として好適である。バッファ層の厚みは、0.01μm～100μm程度が好ましい。

【0019】最初の基板P₀は、少なくとも表面がGaN単結晶であるものを用いる。即ち、全体が実質的にGaNだけからなるGaN単結晶の単独の基板、または、GaN単結晶層をバッファ層形成側の表面に有するような、表面だけがGaN単結晶であるような基板である。後者の場合、GaN単結晶層を担持する基材物質としては、GaN単結晶の成長温度(1000～1100°C)に対する耐熱性が良好なもののが望ましく、例えばサファイア結晶基板、S1基板、水晶、ZnO基板、SiC基板などが例示される。これら基材物質上へのGaN単結晶層の形成は、MOVPE法、MBE法などによる非平衡反応に基づくヘテロエピタキシャル成長法によって行うことができる。

【0020】[GaN単結晶の製造実験および品質確認実験] 次に、本発明のGaN単結晶の製造方法によって実際にGaN単結晶を製造し、その品質を確認した結果を示す。

実験例1

本実験例では、上記本発明のGaN単結晶の製造方法における結晶成長サイクルを繰り返す方法として、図1における工程2に示すように、最初の基板P₀上にバッファ層およびGaN単結晶を順次成長させて積層し、最後に各バッファ層を一度に除去してGaN単結晶を分離する方法とした。最初の基板P₀としては、サファイア結晶基材上にMOVPE法によりGaN単結晶層をエピタキシャル成長させた基板を用いた。バッファ層は厚みを0.2μm、材料をZnOとした。結晶成長サイクルは5回繰り返したものとした。結晶成長サイクル各回に形成されるGaN単結晶P₁～P₅の厚みは全て300μmを目指とした。最後に得られたGaN単結晶P₅の半値全幅を測定したところ、29secであり、また、その厚みは305μmであった。

【0021】実験例2

本実験例では、上記実験例1における結晶成長サイクルを繰り返す方法に代えて、図1における工程3に示すように、GaN単結晶がエピタキシャル成長する度に、その前のバッファ層を除去し、新たな基板を常に1枚のGaN単独の単結晶とした以外は、実験例1と全く同様のGaN単結晶の作製を行った。最後に得られたGaN単結晶P₅の品質は、半値全幅が28secであり、ま

た、その厚みは289μmであった。

【0022】実験例3

本実験例では、上記実験例2における最初の基板として、サファイア基板と、AlN（窒化アルミニウム）のバッファ層と、GaN単結晶とからなる3層の基板を用いた以外は、実験例2と全く同様のGaN単結晶の作製を行った。3層の基板の製作工程を簡単に説明する。厚さ300μm、面積5cm×5cmのサファイア結晶基板上に、バッファ層としてAlNをMOVPE法によって厚み500Åまでエピタキシャル成長させ、その状態のままで材料ガスを切替え、同じMOVPE法によってGaN単結晶を厚み2μmまでエピタキシャル成長させて表層とし、サファイア結晶基板と、AlNバッファ層と、GaN単結晶の表層とからなる総厚約302μmの三層構造の基板を得た。本実験によって最後に得られたGaN単結晶P₆の品質は、半値全幅が2.5secであり、また、その厚みは295μmであった。

【0023】実験例4

本実験例では、上記実験例2において、最初の基板P₆として実験例3と同様の3層の基板を用い、GaN単結晶の結晶成長サイクルを繰り返す際の、各サイクルにおけるバッファ層の材料として(BeO)_{0.13}(ZnO)_{0.87}を用いた以外は、実験例2と全く同様のGaN単結晶の作製を行った。本実験によって最後に得られたGaN単結晶P₆の品質は、半値全幅が2.8secであり、また、その厚みは301μmであった。

【0024】実験例5

本実験例では、本発明によるGaN単結晶の品質と比較するために、従来の製造方法によるGaN単結晶の品質を調べた。厚さ300μm、面積5cm×5cmのサファイア結晶基板上に、スパッタリング法によってZnOを材料とする厚さ0.6μmのバッファ層を成膜し、その上にHVP法によってGaN単結晶を厚さ250μmまでエピタキシャル成長させた。このGaN単結晶の品質は、半値全幅が4.20secであった。

【0025】上記実験結果で明らかなように、本発明のGaN単結晶の製造方法は、従来には無い、高品質なGaN単結晶を製造することが可能であり、かつ、GaN単結晶を単独の基板として用いるのに十分な厚みに製造

することが可能であることが確認された。

【0026】本発明の製造方法によって得られる、このような高品質で厚いGaN単結晶は、発光ダイオード(LED)、レーザーダイオード(LD)、スーパーバーミネッセンスダイオード等の半導体発光素子、電子デバイス等の用途に好ましく用いられる。半導体発光素子においては、本発明のGaN単結晶を基板として用いることで、従来の赤色LED等と同じ電極部の構造を有するLED、LD等の製造が可能となる。これらのなかでも特に、青色発光するものは重要である。また、その半導体発光素子の発光の効率はより高いものとなる。

【0027】【本発明によるGaN単結晶を用いたLEDの品質確認実験】本発明の製造方法によって得られたGaN単結晶を基板として用いたLEDを実際に製造し、その品質を確認した。また、従来品質のGaN単結晶、およびサファイア結晶を各々基板とするLEDを製作し、本発明のGaN単結晶を基板とするLEDの品質と比較した。従来品質のGaN単結晶としては、半値全幅が3.00secのものを用いた。LEDの品質は、初期の輝度と寿命について評価した。寿命は、温度85℃湿度85%の雰囲気中において20mAの電流によって2000時間連続発光させた後の輝度を測定し、その輝度の初期の輝度に対する低下率を求め、低下率2%未満をA、低下率2~5%未満をB、低下率5~10%をCと、3つのランクに分けた。LEDの構造は、本発明の製造方法によって得られたGaN単結晶を基板とし、該基板上に、n-AlGaNクラッド層、アンドープのInGaN活性層、p-AlGaNクラッド層を順次成長させてなるダブルヘテロ接合型の構成とした。本発明によるGaN単結晶の基板の品質は、半値全幅が3.0sec、1.00sec、2.50secの3種類である。厚みはすべて280μmである。また、活性層のInGaNの組成比は、In_{0.15}Ga_{0.85}Nと、In_{0.25}Ga_{0.75}Nの2種類とし、各々の組成比のInGaNについて、発光素子を作成し実験を行った。この実験結果を次の表1、2に示す。

【0028】

【表1】

活性層の組成比が $In_{0.16}Ga_{0.75}N$ である LED
の輝度と寿命の比較

基板	FWHM (sec)	初期の輝度 (candela)	寿命
GaN	30	1.8	A
GaN	100	1.4	A
GaN	250	1.2	B
GaN	300	1.1	B
サファイア	—	1.0	C

【0029】

* * 【表2】
活性層の組成比が $In_{0.25}Ga_{0.75}N$ である LED
の輝度と寿命の比較

基板	FWHM (sec)	初期の輝度 (candela)	寿命
GaN	30	2.9	A
GaN	100	2.5	A
GaN	250	2.2	B
GaN	300	2.2	B
サファイア	—	2.0	C

【0030】表1、2に示すように、本発明による高品質なGaN単結晶を基板として用いたLEDは、初期の輝度と寿命の点で、従来のものより優れたLEDであることがわかった。

【0031】また、LDに関しては、次の現象が確認できた。サファイア結晶を基板とする従来のLDでは、サファイア結晶が、へき開面の形成が困難な物質であるために基板面が好ましい鏡面状態とはならず、その基板面上に形成されるGaN系化合物半導体層の面の状態は、基板面の状態に従うため、LDにとって好ましい反射面は形成することができなかった。しかし、本発明によるGaN単結晶は高品質であり十分な厚みを有するため、GaN単結晶を基板として、そのへき開面を得ることが容易になった。また、従来のGaN系化合物半導体を用いたLDでは、結晶品質が劣っているため、電流注入による誘導放出が達成できなかつたが、本発明による高品質なGaN単結晶を基板として用いたファブリ・ペロー型

共振器のストライブルーザーを構成し実験したところ、室温において誘導放出が確認された。

【0032】

【発明の効果】以上詳述したように、本発明のGaN単結晶は、従来にはなかった結晶品質と充分な厚みを同時に備えるものである。また、本発明の製造方法は、そのような高品質で充分な厚みを同時に備えたGaN単結晶を好適に提供することができる。従って、高効率の青色発光を呈するLEDや、紫外線レーザーダイオード、または耐熱性の良好な半導体デバイスを得るために好適なGaN単結晶の基板を提供することできる。また、本発明の製造方法は、GaN単結晶の結晶品質の向上および厚みの獲得だけでなく、高品質なGaN単結晶を効率良く多数枚製造することが可能であり、工業的にも極めて重要な技術である。

【図面の簡単な説明】

【図1】本発明によるGaN単結晶の製造方法の工程の

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一例を示す模式図である。

【符号の説明】

P₀ 最初の基板

P₁ ~ P₂ GaN单結晶

B₁ ~ B_n パッファ層

[图1]

